

A combined XAS and XRD Study of the High-Pressure Behaviour of $GaAsO_4$ Berlinite

JAMES BADRO¹, PHILIPPE GILLET¹, PAUL F. McMILLAN², ALAIN POLIAN³ and JEAN-PAUL ITIÉ³

¹ *Laboratoire de Sciences de la Terre, Ecole Normale Supérieure de Lyon 46, allée d'Italie 69364 Lyon Cedex 07, France.*

² *Materials Research Group in High Pressure Synthesis, Department of Chemistry and Biochemistry, Arizona State University, Tempe, AZ 85287, USA.*

³ *Physique des Milieux Condensés, Université Pierre et Marie Curie, B77 4, place Jussieu 75252 Paris Cedex 05, France.*

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Abstract. – Combined X-ray absorption spectroscopy (XAS) and X-ray diffraction (XRD) experiments have been carried out on $\alpha - GaAsO_4$ (berlinite structure) at high pressure and room temperature. XAS measurements indicate four-fold to six-fold coordination changes for both cations. The two local coordination transformations occur at different rates but appear to be coupled. A reversible transition to a high pressure crystalline form occurs around 8 GPa. At a pressure of about 12 GPa, the system mainly consists of octahedral gallium atoms and a mixture of arsenic in four-fold and six-fold coordinations. A second transition to a highly disordered material with both cations in six-fold coordination occurs at higher pressures and is irreversible.

Introduction. – The mineral quartz ($\alpha - SiO_2$) and its ordered $AlPO_4$ (berlinite) analogue form archetypal tetrahedral framework structures taken by many compounds (GeO_2 , $GaPO_4$, $GaAsO_4$, $AlAsO_4$) which exhibit phase transformations under high pressure. At room temperature, the kinetics of these pressure-induced transitions are slow and metastable crystal-to-crystal (C-C) transitions or pressure-induced amorphization (PIA) processes are observed [1, 2, 3, 4, 5, 6]. The room temperature compression behaviour and PIA of $\alpha - GeO_2$ was studied previously by X-ray diffraction and X-ray absorption spectroscopy (XAS) [7]. The results showed that the germanium coordination rises from four to six through the high pressure transformation. Molecular dynamics (MD) simulations [8, 9, 10, 11, 12, 13, 6, 14] on SiO_2 quartz indicate that the PIA is also associated with a coordination change.

In the case of quartz-like berlinites, it was first thought that $\alpha - AlPO_4$ exhibited the same room temperature and high pressure behaviour as quartz, and underwent PIA at 15 GPa

[15]. A more recent study [16] has shown that under hydrostatic conditions, this transition is not PIA, but a polymorphic crystalline phase transition. The high pressure form is poorly crystallized, and has a very weak X-ray diffraction pattern. It is suggested from MD simulation that the transition is associated with destabilization of the AlO_4 tetrahedron relative to AlO_6 . *In situ* XAS experiments were carried out on the isoelectronic -isostructural compound, $GaPO_4$, at the K edge absorption energy of gallium [17, 18]. The polymorphic phase transition observed at 13 GPa is associated with a four- to six-fold oxygen coordination change observed around gallium atoms. In the present work, we have used combined XAS and XRD methods to study the high pressure behaviour of $GaAsO_4$, and investigate the local environment of both cations.

Experimental. – Powdered $\alpha - GaAsO_4$ [19] was used for these high pressure energy dispersive EXAFS and X-ray diffraction studies. The samples were loaded in a stainless steel gasket with a 200 μm hole diameter and 50 μm initial thickness and high pressures were generated by a membrane driven diamond anvil cell (DAC). For diffraction, three independent experiments were carried out on the DW-11 energy dispersive X-ray diffraction beamline on the DCI ring of the LURE synchrotron facility in Orsay, France, using argon and silicone oil as pressure transmitting media, and ruby fluorescence as a pressure gauge. XAS was performed on the D11 dispersive XAS [20, 21] beamline at both Ga and As K edges using silicone oil as the pressure transmitting medium.

Results : X-ray Diffraction. – X-ray diffraction spectra recorded as a function of pressure are reproduced in Fig. 1. A polymorphic crystal-to-crystal phase transition is observed to begin [17, 22] around 8.7 GPa. A new diffraction peak is observed between 8.7 and 9.8 GPa, and the remaining peaks begin to broaden. Meanwhile, a fit of the low pressure phase's peaks using the original hexagonal cell yields a negative pressure derivative of the bulk modulus (K') above the transition (fig. 3), which is physically unreasonable and characteristic of a phase mixture. The other very weak and broad peaks of the high pressure phase could be clearly observed only after the hexagonal phase has vanished around 13 GPa. Further pressurization results in a compression of this high pressure structure up to 22 GPa. Above 22 GPa, new peaks appear and superpose with the previous spectrum, showing the onset of a second phase transition. At 28 GPa, the highest pressure reached in this EDX study, the spectrum is that of a very poorly crystallized sample (Fig. 2).

The isothermal equation of state (EOS) obtained from structure refinements using the DICVOL structure refinement program [23] in the low-pressure hexagonal phase (up to 8.7 GPa) and fitted by a third order Birch-Murnaghan EOS shows a bulk modulus $K_0 = 53.4$ GPa with a pressure derivative fixed to $K'_0 = 4$ and a unit cell volume at room pressure $V_0 = 247.2$ Å³ (Fig. 3). This is consistent with previously reported volume data [19, 24], but our equation of state differs considerably from that of Clark *et al.* [22] ($K_0 = 18.6$ GPa and $K'_0 = 18.8$).

Given that no structural data could be extracted from the diffraction patterns and that therefore no structural refinements could be carried out for the two high pressure phases, we chose to combine XAS data in order to analyse the local transformations occurring around both cations.

Results : X-ray Absorption Spectroscopy. – X ray absorption spectroscopy measurements were performed on the system both at the Ga and As K edges and the cation-oxygen distances deduced from the experimental data using the CDXAS package [25] are shown in figure 4; In the low-pressure phase, the Ga-O and As-O bond length moduli can be measured; they both lie around $K_0^{bond} = 320$ GPa with K'_0 set to 4. The large difference with the bulk modulus

($K_0 = 53$ GPa) and the fact that $K_0^{bond} \gg 3K_0^{tet}$ shows that the compression mechanism consists mainly of relative tilting of the tetrahedra (bending of the T-O-T angle) as already reported by vibrational spectroscopy and MD studies [26, 27]. The onset of the polymorphic transition observed by X-ray diffraction occurs around 8 GPa. This corresponds to dramatic bond length changes observed on both edges. The Ga-O mean distance rises rapidly between 8 and 12.5 GPa, at which point the Ga-O bond length corresponds approximately to that for octahedral GaO_6 groups. This is also indicated by the change in shape of the related XANES (X-ray absorption near edge structure) spectra. There is a further slight increase in Ga-O mean distance up to 22 GPa, at which point the structural transformation to six-fold coordinated gallium is complete. Meanwhile, the As-O mean distance also increases between 8 and 12.5 GPa at which point another compression regime appears and the rate of bond length change diminishes, until the corresponding transition is complete at about 22 GPa. These distance variations, *i.e.* the slope of the bond length-pressure curves, indicate the rate of transformation from 4-fold to 6-fold coordinated cations; gallium atoms undergo the coordination change more rapidly with increasing pressure, and therefore at or about 12.5 GPa, the structure mainly consists of six-fold coordinated gallium and arsenic atoms in an average coordination intermediate between four and six.

The gallium K edge energy as a function of pressure reported in figure 5 shows that the transition to the octahedral configuration is accompanied by a 30% increase in the absorption energy (with respect to the K edge absorption level of a *GaAs* standard), and that therefore the different nature of the bonding resulting from modifications of the uppermost electronic shell can be detected by accurate K edge absorption energy measurements.

Discussion : Compression. – It is interesting to note the correlation between XAS and XRD measurements. The cation–oxygen distance starts increasing around 8 GPa, monitored by XAS. Above this pressure, the diffraction lines of the sample start broadening, the background scattering intensity rises, a new diffraction line appears (fig. 1) and the cell parameters and volumes calculated by the data refinement for the hexagonal structure behave unreasonably, in that sense that the mixture of two phases renders the volume fit false, hence a rising difference between the extrapolated EOS and the calculated volume of the hexagonal phase. Around 12-13 GPa, essentially all gallium atoms become 6-fold coordinated, whereas only part of the arsenic is octahedral; At this pressure, a dramatic change is observed by XRD, with the signature of a disordered crystalline material (weak and broad lines, intense broad background). At this pressure, the hexagonal peaks and therefore the associated phase have totally disappeared.

Given these combined observations, we argue that the high pressure phase appears at 8 GPa. Between 8 and 13 GPa, the system is mixed-phase with the average coordination intermediate between 4 and 6 and an average bond length intermediate between l_{tet} and l_{oct} . In this pressure domain, only a small change of the diffraction spectra occurs, because of the superposition of the weak spectrum of the high pressure phase with the intense spectrum of the hexagonal structure. It was not possible to refine the new diffraction peaks. The previously proposed distorted monoclinic structure [22] does not match our diffraction data. Nevertheless it appears from EXAFS that this intermediate phase has twice as much octahedral gallium than arsenic, because the rate of four-fold to six-fold coordination change with pressure is twice as large for gallium than for arsenic (see fig. 4), which seems to confirm one of the structural observations of Clark *et al.*. From our data, we can confirm that the intermediate phase is not of the *InPO₄* type, an expected intermediate structure in berlinite transitions from quartz to rutile-like phases, but belongs to a lower symmetry structure because of the 1/3–2/3 mixture of six-coordinated arsenic and gallium atoms respectively.

Further increase in pressure above 13 GPa reveals another structural transformation. First, continued compression results in a slower rate of change in the arsenic coordination, because the six-coordinated structure of gallium atoms renders the system less compressible. At approximately 22 GPa, all arsenic clusters have transformed into octahedra and the system consists of a pseudo-rutile type structure with fully octahedral cation arrangements, which is indicated by the XANES spectra at the As and Ga K edges which show a clear signature of the well known octahedral clusters [7]. The weak diffraction patterns at these pressures do not permit a structure refinement of this phase. It is not easy to assign a transition pressure, but it is reasonable to suppose that this pseudo-rutile phase appears when arsenic atoms enter their second compression regime around 15 GPa, just after the hexagonal phase has vanished. Above 22 GPa, the system contains the pseudo-rutile phase.

Discussion : Decompression. – The latter assumption, concerning the onset pressure of the second phase transition can be further justified by the decompression history. In fact, one expects the intermediate phase to revert to the original material upon decompression, as observed on berlinite phosphates, whereas the second would only give rise to a partially or totally amorphous sample on pressure quench.

Samples quenched from 15 GPa, *i.e.* after the hexagonal phase has vanished and the second phase has started appearing, undergoes a back-transformation to the original structure (XRD analysis) on decompression. The local atomic structure is tetrahedral but with a partial amorphization of the sample as evidenced by the decrease of the intensity of the XANES features (XAS analysis). On the other hand, the sample decompressed from 25 GPa is completely amorphous and its cations remain mainly in sixfold coordination.

Conclusion. – We have shown that gallium arsenate berlinite undergoes two phase transitions at high pressure and 300 K. The first transformation is a crystalline polymorphic phase transition and is associated, as opposed to phosphates [28, 18, 29, 30], with a local transition from four- to six-fold coordination of *both* cations, *i.e.* the high-pressure phase is not of the $InPO_4$ type. Only part of the As atoms have transformed to high coordination at this point. Further compression leads to full transformation of both cations to six-coordinate, and the structure can be related to a rutile-like phase. As long as this phase has not appeared, samples decompressed allow recovery of the starting crystal. The decompression of systems consisting partly or entirely of this pseudo-rutile phase do not return to the initial structure, and a partly or entirely amorphous material is recovered.

The destabilization of the tetrahedral clusters is confirmed by *in situ* EXAFS. It appears that a large difference exists in the high pressure behaviour of arsenate and phosphate berlinites. In the case of arsenates, both cations undergo a transformation to sixfold coordination at roughly the same pressure whereas the critical pressure needed to destabilize the PO_4 tetrahedra is well above the first transition point at 13–14 GPa for gallium or aluminium, and the two local cationic transitions are totally dissociated. The stability of the PO_4 group is likely responsible for the total reversibility of the phase transition for phosphate berlinites which is not observed for arsenate berlinites (partial or complete amorphization on decompression). Further experiments under simultaneous high pressure–high temperature conditions [29, 31] are under way to fully delineate the phase diagram.

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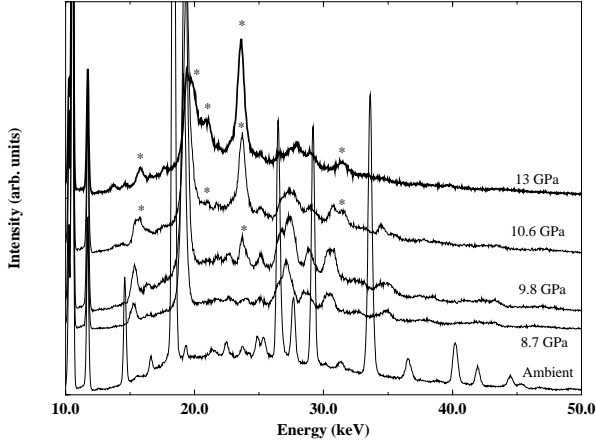


Fig. 1. – Energy dispersive X-ray diffraction spectra for $GaAsO_4$ as a function of pressure. One can note that a phase transition occurs between 8.7 and 9.8 GPa. A new line appears at 24 keV (*-sign), but a total breakdown of the hexagonal structure does not occur until above 10.6 GPa (boldened spectrum). The diffraction angle is $2\theta=11.28^\circ$.

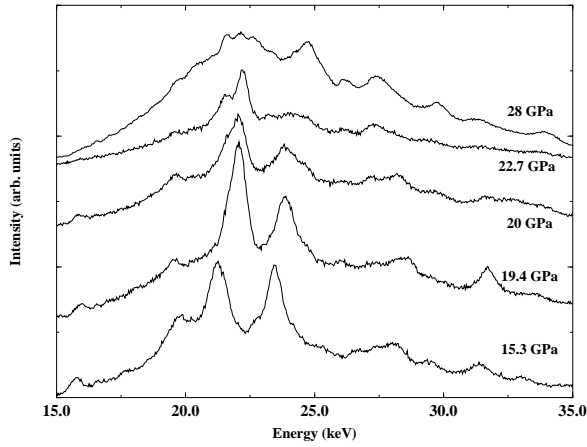


Fig. 2. – Above 20 GPa, new diffraction lines appear in the spectrum as the peaks of the intermediate phase broaden and weaken. They are assigned to the 6-fold coordinated phase observed by EXAFS spectroscopy. Once again, this phase seems to appear at lower pressures but the weakness of its related diffraction lines is such that they are not observed until the preceding intermediate structure's lines weaken themselves.

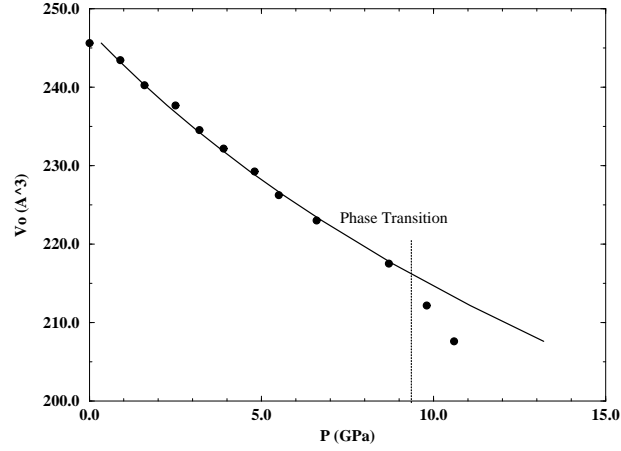


Fig. 3. – Pressure-Volume data points obtained from refinement of the hexagonal structure of the sample in the low pressure phase. The points are fitted by a third order Birch-Murnaghan EOS with $K_0 = 53.4 \text{ GPa}$, K'_0 fixed to 4 and $V_0 = 247.2 \text{ Å}^3$ for the data points up to 8.7 GPa. Above this pressure, the structure distorts and the system is a mixture of two phases thus rendering volume data unreliable and giving yet another signature of the phase transition.

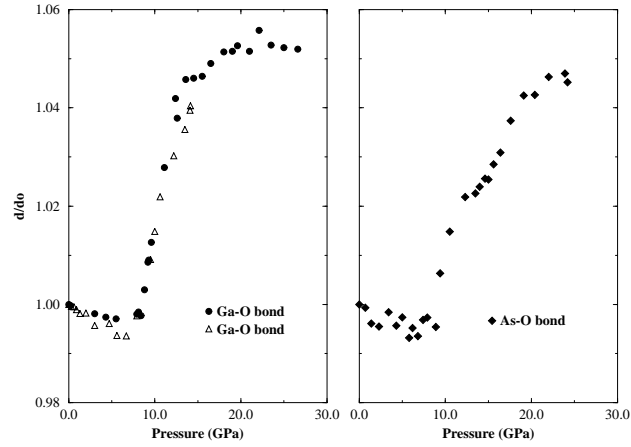


Fig. 4. – Relative bond length (d/d_0) for the Ga-O (two independent experiments) and As-O bonds. It can be seen that there is one compression regime in the 4-to-6 transformation concerning the gallium local environment, but two for arsenic. The second regime appears for arsenic at the pressure for which gallium has become totally octahedral (12-13 GPa).

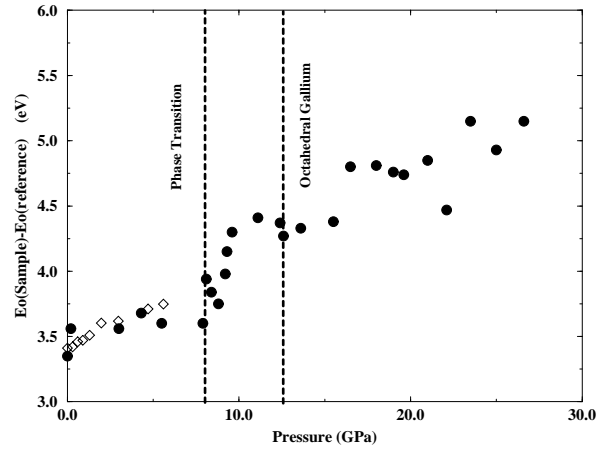


Fig. 5. – Gallium K edge energy displacement as a function of pressure. On the ordinate axis, we report the difference between the K edge absorption energy of gallium in the $GaAsO_4$ sample at pressure P and that of the K edge absorption energy of gallium in a $GaAs$ reference crystal. The transition is accompanied by an increase in the absorption energy. This plot shows that there is notable change in the core level electronic structure associated with the bonding change throughout this transition.